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Model Filled Polymers. VI. Determination of the Crosslink Density
of Polymeric Beads by Swelling

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A new method has been developed to characterize the crosslink density of monodisperse polymeric microbeads by equilibrium swelling on an ultrafiltration membrane, followed by the removal of excess solvent by centrifugation. For polystyrene copolymerized with divinylbenzene and polymethyl methacrylate copolymerized with ethylene glycol dimethacrylate, the mole percent of crosslinked units, approximated, but always exceeded, the mole percent of divinyl monomer. Crosslink densities were varied from 1-11%.			
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Model Filled Polymers. VI. Determination of the Crosslink Density of Polymeric Beads by Swelling

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Introduction

One of the most important structural parameters characterizing crosslinked polymers is \overline{M}_c , the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of \overline{M}_c significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine \overline{M}_c [1-9]. Early research by Flory and Rehner [3, 4] laid the foundations for the analysis of equilibrium swelling. According to the theory of Flory and Rehner [10], for a perfect network,

$$\overline{M}_c = -V_1 \rho_p \frac{(\phi_p^{1/3} - \phi_p/2)}{[\ln(1 - \phi_p) + \phi_p + \chi_1 \phi_p^2]} \quad (1)$$

where,

\overline{M}_c is the number average molecular weight of the polymer between crosslinks

V_1 is the molar volume of the solvent

ρ_p is the polymer density

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ϕ_p is the volume fraction of polymer in the swollen gel

χ_1 is the Flory-Huggins interaction parameter between solvent and polymer

The swelling ratio, s , is equal to $1/\phi_p$. Here, the crosslink density, q , is defined as the mole fraction of crosslinked units [10].

$$q = \frac{M_0}{\overline{M}_c} \quad (2)$$

where, M_0 is the molecular weight of the polymer repeat unit. We have defined q in Equation (2) in order to simplify direct comparison with the mole fraction of divinyl monomers in copolymerization. Other authors [11] define a crosslink density, ν_e , as the number of elastically effective chains, totally included in a perfect network, per unit volume. ν_e is simply related to q . Since,

$$\nu_e = \frac{\rho_p N}{\overline{M}_c} \quad (3)$$

where, N is Avogadro's number. Then,

$$\nu_e = \frac{\rho_p N q}{M_0} \quad (4)$$

Ordinarily, a uniformly swollen polymer sample that is wet with solvent may be dried with absorbent paper and weighed, to determine ϕ_p . This method cannot be applied to polymer microbeads, whose diameter may be less than one micron. We must prevent the loss of polymer microbeads during filtration (for the removal of solvent after swelling) and account for solvent adsorption and inclusion in the large surface and void volumes of collections of beads. Any excess solvent retained by swollen microbeads, in addition to that required for swelling, must be removed for accurate determination of \overline{M}_c .

Using a frozen "sandwich" technique, Miller *et al.* [12] determined the swelling ratios of individual polystyrene microbeads by electron microscopy. Lange [13] determined the swelling ratio of particulate polymers by measuring the volume of swollen particles by sedimentation in an analytical ultracentrifuge. Errede *et al.* [14] developed a technique of fabricating microporous composite films consisting of polystyrene beads, crosslinked with

divinylbenzene and enmeshed in polytetrafluoroethylene microfibers, and characterized the beads reproducibly by the swelling of composite films [15-19]. However, the preparation of such films was a very time consuming process. We will describe simplified techniques for studying the swelling behavior of polymeric microbeads and report typical calibration data.

Experimental Details

Materials

Polymeric microbeads ranging in diameter from 0.2 to 1 μ were prepared by emulsion polymerization in the absence of emulsifier [23]. Polytetrafluoroethylene (PTFE) ultrafiltration membranes with 0.2 μ pores were obtained from Millipore Co. (type FG) and used to enclose the beads in order to prevent loss during swelling. Toluene solvent for polystyrene was analytical reagent from Mallinkrodt Inc. and has a molar volume of 106.3 cm³/mol [20]. For polymethyl methacrylate beads, the solvent used is analytical reagent methyl ethyl ketone obtained from Mallinkrodt, with a molar volume of 89.6 cm³/mol [20]. Hexane was used as non-solvent and is also analytical reagent grade from Mallinkrodt Inc. The density of polystyrene was taken to be 1.05 g/cm³ [20]. The density of polymethyl methacrylate is 1.17 g/cm³ [20].

Swelling

A PTFE ultrafiltration membrane is weighed and inserted in a concave configuration into a metal wire basket, and weighed polymer microbeads placed on the membrane. The basket is suspended within a test tube from a hook attached to a stopper which seals the tube. The basket assembly is soaked in solvent, contained within the tube, which is held in a water bath at a selected swelling temperature.

In order to correct for solvent adsorbed on the surface of beads or contained within the voids between beads, the swelling experiment was first conducted with non-solvent. After about 20 minutes soaking (by which time the sample achieves constant weight), a wet bead sample and PTFE membrane are removed from the wire basket and placed in a centrifuge tube on top of a roll of absorbent paper, in the bottom of the tube, which is then closed with

a stopper. The tube is inserted into a centrifuge (Sorvall, type GLC-2B, DuPont Instrument Co.) with a radius of 10 cm and centrifuged for 5 minutes. Thereafter, the sample and ultrafiltration membrane are removed, placed into a weighing bottle, which was then sealed and weighed. The volume of non-solvent retained was calculated and a correction for trapped solvent derived.

Sample and membrane are dried overnight in a vacuum oven at 80°C, so that all non-solvent has been removed and the sample reacquires its original weight. Following vacuum drying, the sample and membrane are reinserted into the metal wire basket and the entire assembly placed in solvent in a constant temperature bath. Equilibrium swelling was reached within 24 hours. After an identical procedure of centrifugation, the total solvent uptake was determined by gravimetry and corrected as described. The experimental procedure takes about three days, but up to twenty samples are analyzed simultaneously.

The time and speed of centrifugation were selected in order to remove "excess" solvent equilibrating with the swollen bead sample, yet not affect solvent actually swelling the sample, especially for highly swollen, lightly crosslinked, beads. Using crosslinked polystyrene samples, it was observed that the amount of solvent swelling the samples remained constant for 5 minutes centrifugation at speeds ranging from 200 to 800 rpm (although the total solvent uptake and the volume of non-solvent trapped varied with centrifugation speed). Below 200 rpm, the corrected value of included solvent varied sharply with centrifuge speed, while, above 800 rpm, solvent swelling the bead sample was gradually lost. In this research, the centrifugation speed was selected between 300 to 500 rpm, to preclude loss of swelling solvent from lightly crosslinked samples.

The reproducibility of swelling measurements was assessed by repeating tests for four times. The precision of volume fraction determinations of polymer in swollen gels approximated 2% leading to a reproducibility in crosslink density of about 4%. For polystyrene systems, the polymer-solvent interaction parameter was estimated using the following formula [21, 22]:

$$\chi_1 = 0.431 - 0.311\phi_p - 0.036\phi_p^2 \quad (5)$$

For polymethyl methacrylate/methyl ethyl ketone, χ_1 was taken as 0.48, as calculated from

the second virial coefficient from light scattering [24, 25]. Swelling experiments were conducted at 25°C.

It was observed that the weight of swollen samples decreased after prolonged swelling and drying and the presence of some sol in lightly crosslinked polystyrene beads was inferred [6, 7]. Accordingly, polystyrene beads were extracted with toluene for 48 hours, followed by acetone for 24 hours, prior to swelling experiments. The fractions of material extracted ranged from 3.4 to 6.8%. Extracted samples did not, subsequently, decrease in weight during swelling experiments.

Results

The crosslink densities of polystyrene and polymethyl methacrylate beads are reported. Results of swelling measurements on different polystyrene microbeads crosslinked with selected amounts of divinyl benzene (DVB) are listed in Table 1.

Polymethyl methacrylate (PMMA) beads had been crosslinked with either ethylene glycol dimethacrylate (EGDMA) or allyl methacrylate (AMA). The results of swelling measurements on different PMMA beads are summarized in Table 2.

Discussion

In ascertaining the amount of swelling, we have corrected for adsorbed and interstitial solvent by assuming that the volume of excess solvent is equal to the volume of non-solvent retained under identical experimental conditions. Of course, this is only an approximation. However, we suggest that this is a reasonable assumption in order to account for an, otherwise, elusive quantity.

For the swelling of PS beads, it is observed (Table 1), that the mole fraction of crosslinked units, q , always exceeds the mole fraction of DVB in copolymerization with styrene. Several explanations are possible. Since crosslinked PS networks were extracted with toluene and acetone, prior to swelling, it is likely that soluble linear and branched materials are lost. These include very lightly crosslinked PS. As a result, the apparent crosslink density of the extracted gel would be elevated.

Subsequent swelling studies in our laboratories have shown that the crosslink density of the PS networks varies with conversion and, ordinarily, is highest at low conversion. This results from batch copolymerization, in which the reactivity of DVB is higher than that of styrene in copolymerization [22, 26-30]. Although, the samples studied are, usually, of high conversion, it is possible that some range of crosslink density is observed.

For the swelling of PMMA networks, we observed that EGDMA was always a more efficient crosslinking comonomer than AMA. Since AMA is not "symmetrical" and includes allyl, as well as, methacrylate, functional groups, it is likely that allyl is less reactive. As a result, during copolymerization with methacrylates, pendant allyl groups are less effective in crosslinking. Indeed, we have observed that the presence of EGDMA increases the rate of copolymerization, while the addition of AMA reduces the rate of reaction. However, although the efficiency of crosslinking was reduced in the copolymerization of methacrylate with allyl methacrylate, the premature coagulation of the emulsion (during reaction), was also reduced.

Again, with EGDMA, the mole fraction of crosslink units, q , exceeds the mole fraction of EGDMA in copolymerization. Perhaps, as with PS networks, the extraction of soluble linear and branched methacrylate chains, in this case, during swelling, leads to an overestimation of the actual crosslink density.

Unsuccessful attempts were made using spectroscopic techniques to detect unreacted unsaturation in the uncrosslinked networks, corresponding to pendant vinyl, methacrylate or allyl groups. It is possible that such groups may have disappeared by side reactions. In any case, the very small concentration of possible pendant groups may preclude spectroscopic analysis.

Conclusions

A simplified technique has been developed for characterizing the crosslink density of monodisperse polymeric beads by equilibrium swelling. This technique involves swelling beads on a PTFE ultrafiltration membrane, correcting for excess solvent, adsorbed or included, by comparison with non-solvent, and removing excess solvent by centrifugation. For PS beads, the mole percent of crosslinked units, approximated, but always exceeded, the

mole percent of DVB in copolymerization with styrene. Here, the crosslink density was varied from 1-11%. For the crosslinking of PMMA beads, EGDMA was a more efficient crosslinking comonomer than AMA. Here, the crosslink density approximated, but slightly exceeded, the mole percent of EGDMA comonomer. The reproducibility in crosslink density measurements by this technique approximated 4%.

Research is in progress on the variation and control of crosslink density in polymeric beads with conversion.

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Table 1. Swelling of Polystyrene Beads

DVB mole%	s	ϕ_p	\overline{M}_c	q mole%
1	5.13	0.195	6.8×10^3	1.52
2	4.23	0.236	4.2	2.51
2	4.52	0.221	4.9	2.11
5	3.12	0.321	1.8	5.76
5	3.04	0.329	1.7	6.19
10	2.52	0.398	0.97	10.70
10	2.47	0.404	0.93	11.26

Table 2. Swelling of Polymethyl Methacrylate Beads

Crosslinker mole%	s	ϕ_p	\overline{M}_c	q mole%
5% EGDMA	2.54	0.393	1.7×10^3	5.73
5% EGDMA	2.63	0.380	1.9	5.14
5% AMA	2.99	0.335	2.91	3.44
5% AMA	2.99	0.334	2.92	3.43

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